

Determination of the degree of substitution (DS) of mixed cellulose esters by elemental analysis.

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ABSTRACT

Equations for transforming the results of elemental analysis (EA) into degree of substitution (DS) values for aliphatic cellulose esters were developed. The equations allow to determine the DS of cellulose derivatives bearing not only one but also two different acyl substituents. Error transmission studies revealed that the accuracy of the DS-values for a pure sample depends on both the number of carbon atoms in the substituents and on the uncertainty of the EA, especially from the hydrogen content. This method provides accurate DS-values (± 0.10 in most cases) if H-content determinations are within $\pm 0.1\%$.

INTRODUCTION

Heterosubstituted (mixed) cellulose esters are of particular interest in several fields. The combination of two or more types of acyl groups grafted to the same cellulose backbone confers additional properties compared to the homosubstituted cellulose esters. For instance, cellulose acetates are polymers that require a plasticizer for processing by thermal molding, whereas cellulose acetate-propionate and cellulose acetate-butyrate are thermoplastic materials by themselves. It has also been demonstrated that the mixed cellulose esters containing acetyl and fatty acyl groups show better mechanical properties than the simple fatty cellulose esters (Vaca-Garcia *et al.*, 1998) and maintain similar hydrophobic properties. All of these characteristics depend not only on the nature of the substituents, but also on their individual degree of substitution (DS).

The DS of cellulose mixed esters is usually determined either by integration of

the proton signals in a ^1H -NMR spectrum (Lowman, 1998; Buchanan *et al.*, 1987) or by the aminolysis of the ester groups with pyrrolidine followed by a chromatographic separation of the fragments (Mansson and Samuelson, 1981). However, these techniques present certain limitations. On the one hand, the NMR method requires a complete solubilization of the sample in a deuterated solvent; therefore, most cellulose esters with low DS cannot be analyzed by this technique. On the other hand, the pyrrolidinolysis method (and other hydrolytic techniques) may not be quantitative when analyzing long-chain or highly substituted cellulose esters due to steric hindrance. Not to mention that the unavailability of appropriate standards (1-acylpyrrolidines) is not a negligible difficulty. A comparison study between the NMR and the pyrrolidinolysis methods was recently carried out by Samaranayake and Glasser (1993).

Distinct from these methods, the elemental analysis (EA) is worth considering for the DS determination of cellulose esters and derivatives because of its simplicity. The reactions involved are quantitative and practically independent of the physical and chemical characteristics of the sample. This approach has been used by Otto (1994) to calculate the DS of amylose esters and other derivatives from their carbon content. The equations developed by Otto can certainly be applied to the analysis of the corresponding cellulose derivatives since both polysaccharides possess the same molecular formula. In their simplest form, Otto's equations allow to know the DS of homosubstituted derivatives. In their more general form, they can calculate the DS of one particular substituent in a heterosubstituted derivative as long as all the other substituents are already perfectly quantified (case rather infrequent).

To our knowledge, EA has never been applied to the overall DS-determination of heterosubstituted cellulose (or amylose) esters (or other derivatives). No

methodology or equations are available to correlate multiple DS-values with the carbon, hydrogen and oxygen contents of the polysaccharide derivative. It was the objective of the present study to develop such equations and to investigate the reliability of the obtained DS-values by calculating the transmission of error from EA analysis to DS-evaluation.

METHODS

Deduction of the equations

Let us consider a cellulose ester (Scheme 1) resulting from the acylation with i different saturated carboxylic acids. Its molecular formula is thus represented by:

$$\text{C}_{6+\sum DS_i \cdot n_i} \text{H}_{10+\sum 2 \cdot DS_i (n_i-1)} \text{O}_{5+\sum DS_i}$$

where DS_i is the degree of substitution of the i^{th} acyl substituent containing n_i carbon atoms.

Such molecular formula represents the average non-terminal anhydroglucose units of the cellulose ester. Terminal units are arbitrary neglected. The error caused by this consideration is less than 1% when the degree of polymerization (DP) is higher than 11. For DP-values as high as 120, which are reasonable values for standard cellulose derivatives, error is reduced to less than 0.1%.

From the molecular formula, we can establish equations for the carbon, hydrogen and oxygen contents (C , H , O), expressed as a fraction, as a function of DS_i and n_i .

$$C = \frac{12.011 \cdot (6 + \sum DS_i \cdot n_i)}{12.011 \cdot (6 + \sum DS_i \cdot n_i) + 1.008 \cdot (10 + \sum 2 \cdot DS_i (n_i - 1)) + 15.999 \cdot (5 + \sum DS_i)} \quad \{1\}$$

$$H = \frac{1.008 \cdot (10 + \sum 2 \cdot DS_i \cdot (n_i - 1))}{12.011 \cdot (6 + \sum DS_i \cdot n_i) + 1.008 \cdot (10 + \sum 2 \cdot DS_i (n_i - 1)) + 15.999 \cdot (5 + \sum DS_i)} \quad \{2\}$$

$$O = \frac{15.999 \cdot (5 + \sum DS_i)}{12.011 \cdot (6 + \sum DS_i \cdot n_i) + 1.008 \cdot (10 + \sum 2 \cdot DS_i (n_i - 1)) + 15.999 \cdot (5 + \sum DS_i)} \quad \{3\}$$

In this set of equations, only two of them are independent. The third equation is automatically fixed by the intrinsic relation:

$$C + H + O = 1 \quad \{4\}$$

Therefore, a maximum of two unknown values can be resolved through these equations. In other words, by using EA, it is possible to determine the individual DS-values of cellulose esters having two different kinds of substituents.

In the case of simple esters, only one kind of substituent is present ($i = 1$). Then, equation {1} can be solved to yield:

$$DS = \frac{5.13766 - 11.5592 \cdot C}{0.996863 \cdot C - 0.856277 \cdot n + n \cdot C} \quad \{5\}$$

In the case of two different substituents ($i = 1, 2$), the unknown DS_1 and DS_2 -values are determined by simultaneous treatment of equations {1} and {2}, (C and H are obtained together in a common C-H-N elemental analysis). The solution of the equation system was obtained with the *Mathematica*[®] software.

$$DS_1 = \frac{\begin{bmatrix} n_1 \cdot (-2.20309 + 9.66691 \cdot C - 8.28476 \cdot C^2 - 15.2806 \cdot H + 17.8454 \cdot C \cdot H) + \\ n_2 \cdot C \cdot (-0.427466 + 3.27445 \cdot C - 16.5344 \cdot H) + \\ n_1 \cdot n_2 \cdot (0.367181 - 3.24147 \cdot C + 3.28476 \cdot C^2 + 14.2026 \cdot H - 16.5864 \cdot C \cdot H) + \\ C \cdot (2.5648 - 8.25877 \cdot C + 17.7895 \cdot H) \end{bmatrix}}{\begin{bmatrix} (n_1^2 - n_1 \cdot n_2) \cdot (0.367181 - 1.28509 \cdot C + C^2 + 2.54677 \cdot H - 2.97424 \cdot C \cdot H) + \\ C \cdot (n_1 - n_2) \cdot (-0.427466 + 0.996863 \cdot C - 2.96491 \cdot H) \end{bmatrix}}$$

{6}

$$DS_2 = \frac{-2.57287 + 8.28476 \cdot C - 17.8454 \cdot H + n_1 \cdot (0.428811 - 3.28476 \cdot C + 16.5864 \cdot H)}{(0.428811 - C + 2.97424 \cdot H) \cdot (n_2 - n_1)}$$

{7}

RESULTS AND DISCUSSION

Principle of the technique

The mathematical simultaneous resolution of equations {1} and {2} can be represented graphically. The example of a particular cellulose acetate-propionate (CAP) is shown in Figure 1. The intersection of the C iso-content line and the H iso-content line (C and H values found by EA) defines the composition ($DS_{acetate}$ and $DS_{propionate}$) of the considered cellulose ester.

From Figure 1 and from the complete plot of the C and H iso-content lines (Figure 2), it is evident that a given CAP, with particular $DS_{acetate}$ and $DS_{propionate}$ values, has a *unique pair* of C and H -values. Such values are distinct and cannot be imitated by another combination of $DS_{acetate}$ and $DS_{propionate}$ values. This "non-emulation" principle is essential to the validation of the method.

It is important to note that also partially-substituted cellulose esters are actually

considered. EA provides the DS_1 and DS_2 values from equations {6} and {7}, and the number of non-derivatized hydroxyl groups per anhydroglucose unit (DS_{OH}) is obtained from the relation:

$$DS_1 + DS_2 + DS_{OH} = 3$$

When plotting C and H -lines for other mixed cellulose esters, similar graphs are obtained in which the slope of the lines and the displayed magnitudes vary. Figure 3 shows the case of acetate-octanoate cellulose esters, which are interesting thermoplastic polymers.

At a first glance, this method would seem to be general. However, some particular cases can arise. For example, when n_1 and n_2 are both high close values (e.g., 18 and 19), the C and H -lines become almost parallel (Figure 4). Graphically, finding a particular intersection in such a case can be very difficult. From a mathematical point of view, the results obtained can vary greatly with a little deviation in one of the content values. Thus, the DS-determination becomes highly sensitive to EA errors. In the extreme case, the C and H -lines become parallel, with slopes equal to -1 , when both n_1 and n_2 tend to infinite, making thus impossible the differentiation of the two substituents. Although such long-chain mixed esters are exceptional in conventional cellulose research, this example demonstrates us that it is important to evaluate the variations of the calculated DS-values as a function of both the EA experimental error and the nature of the substituents.

Accuracy

Let us consider the experimental error in EA measurements through the estimation of the standard deviation (σ) in a significant number of EA measurements.

State-of-the-art EA equipments can provide σ -values less than 0.001 in an absolute fraction scale. For our calculations, we will use $\sigma = 0.001$.

Deviations in the DS-determination were calculated on various theoretical cellulose mixed acetates and cellulose mixed propionates bearing another acyl group ($n_2 = 3$ to 18) and being equally substituted, i.e., $DS_1 = DS_2 = 1.5$. Then, by fluctuating the C and H exact theoretical values to $C \pm 0.001$ keeping H constant and to $H \pm 0.001$ keeping C constant, the inexact DS_1 and DS_2 -values were thus computed. From the latter, standard deviations for each substituent (σ_1 and σ_2) were calculated.

Table 1 presents the σ_1 and σ_2 -values for the most common mixed cellulose esters bearing acetate groups. The comparison of the values shows that higher variations are systematically obtained in the DS-determination of the acetate substituent. Differences can be as low as in the case when C varies in a cellulose acetate-propionate ($\sigma_{\text{acetate}} = 0.036$ vs. $\sigma_{\text{propionate}} = 0.035$) or as high as in the case when H varies in acetate-hexanoate ($\sigma_{\text{acetate}} = 0.338$ vs. $\sigma_{\text{hexanoate}} = 0.009$). The plot of these data (Figure 5) shows clearly that the variations of σ_1 or σ_2 are not linear when changing the number of carbon atoms in the longer substituent. Moreover, the standard deviations in acetyl and alkyl groups resulting from experimental error in the H -determination (AH and KH respectively in Figure 5) present a minimum value for cellulose acetate-valerate ($n_2 = 5$). Errors in DS-determination resulting from experimental error in the C -determination (AC and KC in Figure 5) are basically lower than 0.1 and present a minimum value for the evaluation of $DS_{\text{hexanoate}}$ in cellulose acetate-hexanoate.

Table 2 and Figure 6 show the σ_1 and σ_2 -values for the most common cellulose propionate-alkanoate esters. For the latter, the determination of the alkyl substituent becomes overall more precise than in the case of the acetate-bearing mixed esters. On

the contrary, the determination of the shortest substituent (propionate), becomes slightly less precise than in the case of acetate. In the series of the cellulose propionate-alkanoate esters, the propionate-octanoate and the propionate-decanoate esters show the smallest sensitivity to the \mathbf{H} -variations. Similarly, the propionate-butyrate and the propionate-valerate esters show the smallest variations in the DS-determination when \mathbf{C} varies.

From a general point of view, it can be remarked in Figures 3 and 4 that only the DS-determination of the smallest substituent (acetate or propionate) is singularly sensitive to changes in \mathbf{H} . All of the other DS-deviations remain practically in the same order of magnitude (less than 0.1 for a 0.001 variation in \mathbf{C} or \mathbf{H}).

It is important to remind that these determinations were effectuated by considering $\sigma_{\mathbf{C}} = \sigma_{\mathbf{H}} = 0.001$. The obtained σ_1 and σ_2 -values can be extrapolated proportionally to different $\sigma_{\mathbf{C}}$ or $\sigma_{\mathbf{H}}$ -values, as it was found that they vary linearly up to $\sigma_{\mathbf{C}}$ or $\sigma_{\mathbf{H}} = 0.100$. The example below illustrates the complete utilization of this method for a practical case.

Example

The EA of a purified sample of cellulose acetate-octanoate ($n_1 = 2$; $n_2 = 8$) gave the following results: $\mathbf{C} = 0.54072 \pm 0.00153$; $\mathbf{H} = 0.06804 \pm 0.00031$ when repeated three times. By introducing the average values in equations {6} and {7} we obtain: DS_1 (acetate) = 1.95; DS_2 (octanoate) = 0.47. In Table 1 we read at $n_2 = 8$ the standard deviations for each substituent. These values need to be corrected using the real $\sigma_{\mathbf{C}}$ and $\sigma_{\mathbf{H}}$ values, and added to obtain the total standard deviation for each substituent (variation due to \mathbf{C} + variation due to \mathbf{H}):

$$\sigma_1 = 0.068 \cdot (0.00153/0.001) + 0.357(0.00031/0.001) = 0.214;$$

$$\sigma_2 = 0.027 \cdot (0.00153/0.001) + 0.029 \cdot (0.00031/0.001) = 0.050.$$

Then, the final report should read:

$$DS_{acetate} = 1.95 \pm 0.21; DS_{octanoate} = 0.47 \pm 0.05;$$

Furthermore, the unsubstituted OH groups can also be estimated:

$$DS_{OH} = 3 - 1.95 - 0.47 = 0.58$$

The relative precision of the calculated DS-values is thus about 10%.

Further considerations

Other sources of error: The presented method (equations and accuracy calculations) considers pure cellulose ester samples. It is obvious that impurities will produce interferences in the EA and will cause the results to be incorrect. Even water can be a major error source and must be carefully avoided. Hence, the control of the impurities is the main limitation for this technique.

Special derivatives: If the substituents contain atoms different from C, H or O, (nitrates, methylsilyl groups, etc.) supplementary equations can be established and therefore the DS-determination of a third or fourth substituent becomes possible.

CONCLUSION

Elementary analysis provides an easy and powerful method for the DS-determination of homosubstituted and heterosubstituted (mixed) esters of cellulose or amylose. Samples in the whole DS-range can be analyzed and the accuracy of the method depends essentially on the reproducibility of the EA results provided a pure

sample is analyzed. A state-of-the-art EA apparatus is able to provide DS-determinations to about 10% uncertainty in a relative scale.

Cellulose acetate-valerate, acetate-hexanoate, propionate-butyrate, propionate-valerate, propionate-octanoate and propionate-decanoate showed particular stability against experimental errors in the EA. The variations in EA, especially in the hydrogen content, have a stronger effect on the DS-deviation for the smallest substituent than for the largest one.

The methodology developed in this study can be applied to the analysis of other cellulose or amylose mixed derivatives such as ethers or even ester-ethers by adapting the initial molecular formula and solving the set of equations.

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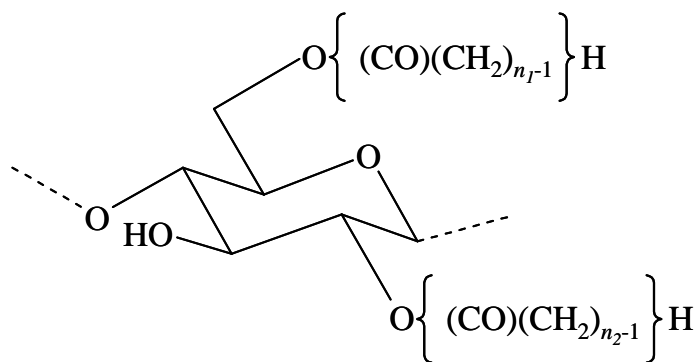
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n_2 (alkyl)	When $\sigma_C = 0.001$		When $\sigma_H = 0.001$	
	σ_1 (acetate)	σ_2 (alkyl)	σ_1 (acetate)	σ_2 (alkyl)
3	0.036	0.035	0.411	0.123
4	0.047	0.028	0.346	0.039
5	0.054	0.027	0.336	0.008
6	0.059	0.026	0.338	0.009
7	0.064	0.026	0.346	0.020
8	0.068	0.027	0.357	0.029
10	0.076	0.029	0.383	0.042
12	0.084	0.030	0.412	0.053
14	0.091	0.032	0.442	0.063
16	0.099	0.034	0.472	0.072
18	0.107	0.037	0.504	0.080

Table 1. Standard deviations (σ) of DS for each substituent in cellulose acetate-alkanoates as a function of the σ of carbon and hydrogen contents given by elemental analysis and the number of carbon atoms in the alkyl group.

n_2 (alkyl)	When $\sigma_C = 0.001$		When $\sigma_H = 0.001$	
	σ_1 (propionate)	σ_2 (alkyl)	σ_1 (propionate)	σ_2 (alkyl)
4	0.081	0.001	0.679	0.352
5	0.076	0.010	0.503	0.156
6	0.076	0.014	0.455	0.089
7	0.078	0.017	0.440	0.053
8	0.081	0.019	0.437	0.031
10	0.088	0.022	0.451	0.002
12	0.094	0.025	0.467	0.017
14	0.101	0.028	0.492	0.032
16	0.108	0.030	0.520	0.044
18	0.115	0.033	0.548	0.055

Table 2. Standard deviations (σ) of DS for each substituent in cellulose propionate-alkanoates as a function of the σ of carbon and hydrogen contents given by elemental analysis and the number of carbon atoms in the alkyl group.



Scheme 1. One of the possible monomer units in a cellulose mixed ester. The part in brackets represents the increase in mass due to the saturated aliphatic substituents.

n_1, n_2 : number of carbon atoms in the acyl group.

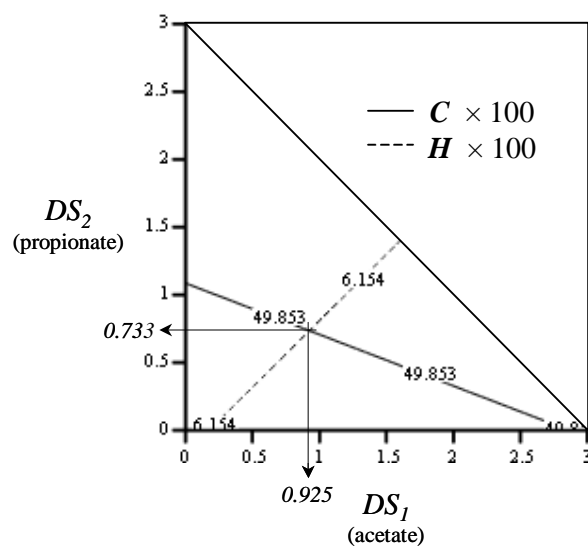


Figure 1. Graphical solution for the DS-determination from the carbon and hydrogen contents (C and H). Example of a cellulose acetate-propionate with 49.853 %C and 6.154 %H. A unique solution exists giving $DS_{acetate} = 0.925$ and $DS_{propionate} = 0.733$.

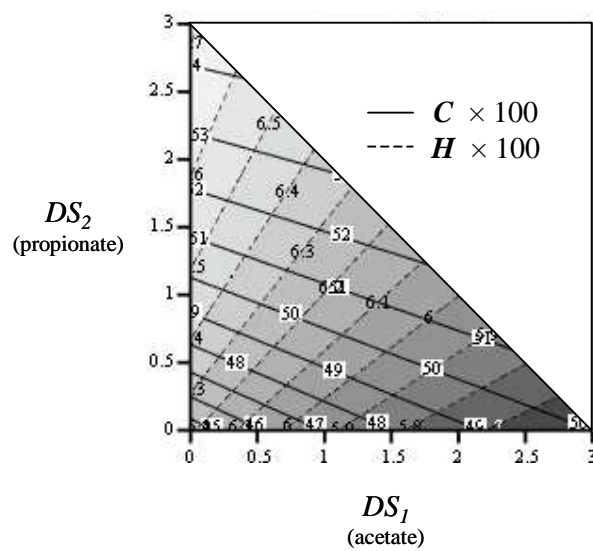


Figure 2. Carbon and hydrogen iso-content lines for the analysis of any cellulose acetate-propionate.

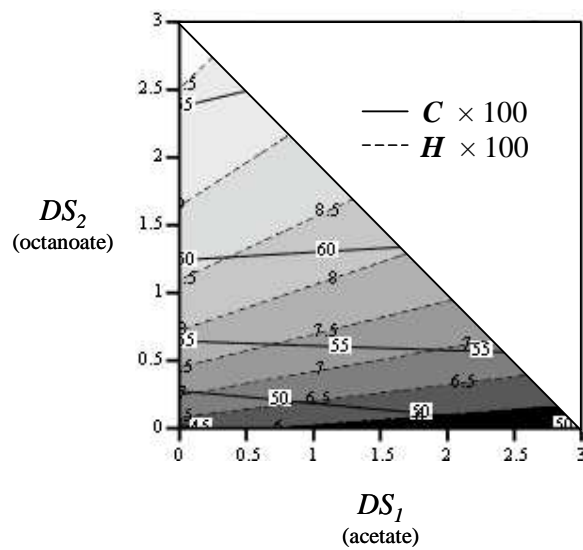


Figure 3. Carbon and hydrogen iso-content lines for the analysis of cellulose acetate-octanoates.

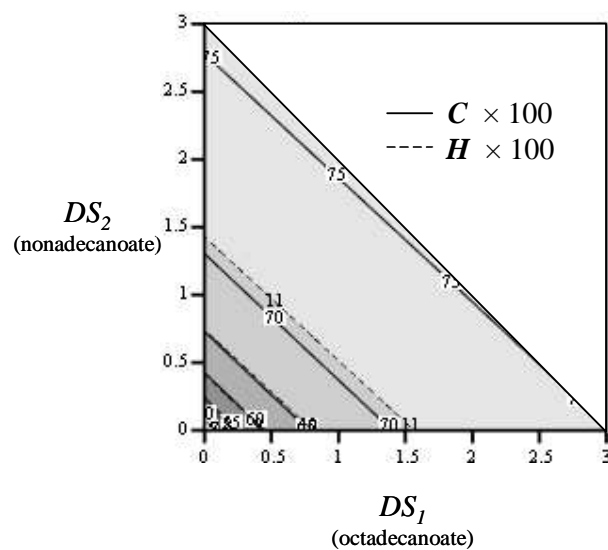


Figure 4. Carbon and hydrogen iso-content lines for the analysis of cellulose stearates-nonadecanoates. DS-determinations become highly error-sensible when both n_1 and n_2 are high close values.

Figure 5. Carbon and hydrogen iso-content lines for the analysis of cellulose stearates-nonadecanoates. DS-determinations become highly error-sensible when both n_1 and n_2 are high close values.